One Step Microwave Combustion Synthesis and Sintering of Coated Intermetallics – Numerical Simulation

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Abstract – The excess heat released by combustion synthesis reactions, arising specifically from the enthalpy of formation of the product(s), is usually dissipated toward the surrounding environment. The aim of the present work is to propose an innovative adaptation of this process in which such high energy and high temperature conditions are proficiently exploited to promote microwave assisted sintering or an additional combustion synthesis (CS) of a further phase deposited over the reactive specimen. As concerns microwave (MW) ignition, the excess heat deriving from combustion synthesis reactions of metallic powders, leading to aluminide-based intermetallic substrates, has been exploited to enhance the direct microwave absorption by a room-temperature low-loss ZrO_2 coating due to the rapid increase in the effective dielectric loss factor with temperature. This makes microwave assisted sintering possible; the same approach has been used to enhance the MW assisted CS of a different intermetallic-based coating. A multiphysics numerical simulation approach has been used in order to highlight the uniqueness of microwaves in obtaining, in a single step, ceramic and intermetallic coated intermetallic substrates, following the aforementioned preparation strategy.

Introduction

Combustion synthesis (CS) is an exothermic process in which the high temperatures involved arise from the formation enthalpy of the products of a reaction occurring generally between powdered reactants. If the enthalpy value is high enough, the reaction is self-sustained and does not require any further external energy source in addition to the energy contribution required to reach the ignition temperature (T_{ig}). The CS process encompasses two different sub-processes depending on the way in which the ignition is reached. In the Self-propagating High-temperature Synthesis (SHS) way of ignition, the reaction is ignited at one end of the reactive specimen and it self-propagates throughout the whole sample, while in the thermal explosion (TE) mode the whole volume of the reactive mixture is heated uniformly up to the ignition temperature allowing the reaction to take place simultaneously in the entire sample [1, 2].

A large variety of materials can be produced using the CS technique, with several advantages over more conventional preparation strategies [3]. Among these materials, intermetallic compounds and phases – particularly aluminides – are considered to have great potential for structural as well as coating applications, mainly due to an excellent compromise between low weight and good mechanical properties at high temperatures [4].

This work is focused on two different intermetallic systems: the β-NiAl intermetallic phase, and the γ-TiAl intermetallic-based alloy. Particularly, high temperature oxidation resistance of both of these materials can be greatly and easily improved by coating, such as partially yttria stabilized zirconia thermal barrier coating. Moreover, the γ-TiAl intermetallic based alloy, unlike the β-NiAl intermetallic phase, is known to be unable to form a durable protective alumina scale [5]. In order to maintain a protective alumina scale for long times, a β-NiAl coating applied in order to suppress the diffusion of Ti from TiAl toward the outer layer is considered a promising and reliable solution [6, 7].

The aim of this paper is to obtain a ceramic and intermetallic-coated intermetallic based substrate by a single combustion synthesis step ignited by microwaves. In detail, the excess heat released by the combustion synthesis in the systems Ni-Al and Ti-Al has been exploited not only to obtain the desired intermetallic substrate through a self-sustaining reaction, but also to sinter a zirconia layer previously deposited by electrophoretic deposition. Moreover, a β-NiAl coated γ-TiAl based alloy has been realized by a single MW-ignited combustion synthesis experiment.

A multiphysics numerical simulation approach was also used in order to underline the uniqueness, and of course the advantages, of the microwave ignition technique in obtaining, through the single combustion synthesis experiment, zirconia- and β-NiAl-coated intermetallic based substrates. The combined effect on the coating sintering or synthesis process of the heat released by the CS (occurring in the underlying substrate) and of the direct microwaves absorption by the coating (which greatly increases while its temperature increases) on the samples microstructure and properties will be shown and discussed.

Technique

Elemental Ni (~ 3 μm, 99.7% purity), Al (-200 mesh, 99% purity) and Ti (-325 mesh, 99.98% purity) were purchased from Sigma Aldrich (Milan, Italy), while submicrometric monoclinic ZrO_2 powders from Colorobbia S. p. A. (Italy).

The combustion synthesis experiments were conducted in a microwave TE_{103} single mode applicator (WR-340 waveguide geometry) operating at a frequency of 2.45 GHz. Ignition of the reactive specimens was reached by applying a MW forward power of 1.2 kW.

ZrO_2 coated intermetallic compounds. ZrO_2 powders were deposited over a mixture of compacted (150 MPa) reactive Ni+Al (50:50 at.%) or Ti+Al (50:50 at.%) powders by means of electrophoretic deposition. Aqueous suspensions were prepared by adding the ZrO_2 powders to bi-distilled water (0.1-1 wt.%) using citric acid as a charging agent. Anodic electrophoretic deposition of zirconia powders was realized by applying a voltage of 10 V for a deposition time of approximately 10 min. ZrO_2 coated reactive metallic specimens were positioned in the centre of the MW single mode applicator, on a metallic disc in order to separate the sample from an auxiliary SiC co-absorber, which has been used in some experiments.

β-NiAl coated γ-TiAl based intermetallic alloy. The two different (2 g of Ni+Al, 50:50 at% and 4 g of Ti+Al, 50:50 at%) cylindrical and reactive pellets (representative of the coating and of the substrate respectively) were separately prepared by cold uniaxially pressing at 150 MPa. A “sandwich-like” joining couple was then prepared by positioning the reactive specimens one above the other, and was positioned in the centre of the MW single mode applicator over a refractory basement. In order to promote adhesion, interdiffusion, and even reaction between the substrate and the coating, a slight pressure of 0.15 MPa was applied by means of a refractory ram during the combustion synthesis experiment.

Numerical simulation procedure. The multiphysics numerical simulation presented in this work was performed using the commercial Finite Element software *COMSOL Multiphysics* v. 3.5a. The simplified model developed considers the thermal and dielectric material properties as functions of temperature and of the degree of completion of the reaction leading to the intermetallic substrate, and it accounts for the subsequent electromagnetic field distribution variations induced by such changes in a fully coupled model. This approach allows investigation of the beneficial effects of using the excess heat of the combustion synthesis to improve the capability of the coating to absorb microwaves, and thus to be rapidly sintered (or ignited) by

Fig. 1. Metallic powder compact (grey region) electrophoretically coated by a "green" zirconia particle (white region) coating.

direct microwaves absorption and by the exposure to the high temperatures of the CS occurring in the underlying substrate.

Results

Anodic EPD of sub-micrometric zirconia powders on Ni+Al and Ti+Al reactive deposition electrodes allowed us to obtain a dense and uniform deposit approximately 100 μm thick as shown in Figure 1.

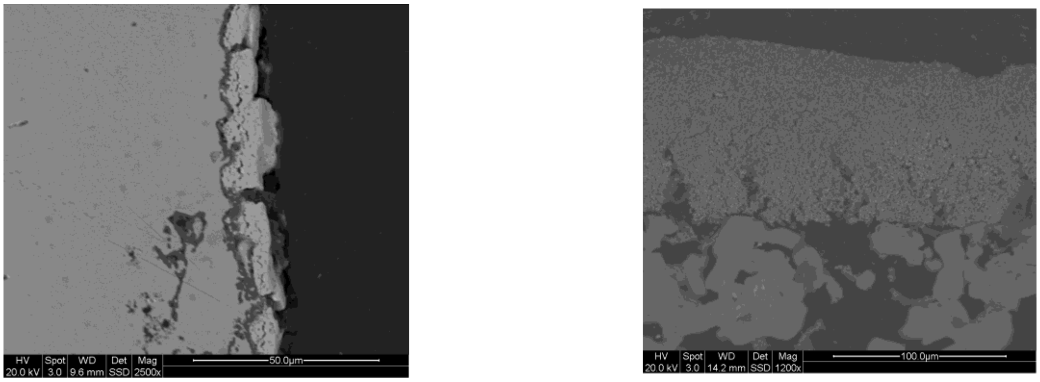
Figure 2 shows typical microstructures of the samples after microwave ignition of the CS, which occurred approximately after 25 seconds. In particular, the cross sections of ZrO_2 coated NiAl intermetallic and ZrO_2 coated TiAl based intermetallic alloy samples are reported in Figs. 2(a) and 2(b) respectively.

A simplified model of the microwave assisted CS of intermetallic compounds has been reported previously, but it was limited in the bidirectional coupling of the electromagnetic and thermal modules, while the heat release was approximated by adding a temperature-dependent term proportional to the load volume [8]. Such a model already allowed underlying the uniqueness of microwaves as an ignition source for combustion synthesis reactions, in directly transferring energy to the reactive specimen [8].

A more complex model has been developed in order to take into account the real kinetics of the CS reactions as well as the temperature dependence of the zirconia coating permittivity, in agreement with the data from [9]. Indeed, the combustion synthesis reaction in the underlying intermetallic substrate allows increasing the ZrO_2 temperature up to a value at which its microwave absorption becomes significantly higher due to the rapid increase in its effective dielectric loss factor [10]. Microwave power dissipation and temperature in the Zirconia coating before, during (at 23 seconds), and after Ni+Al combustion synthesis are shown in Fig. 3(a).

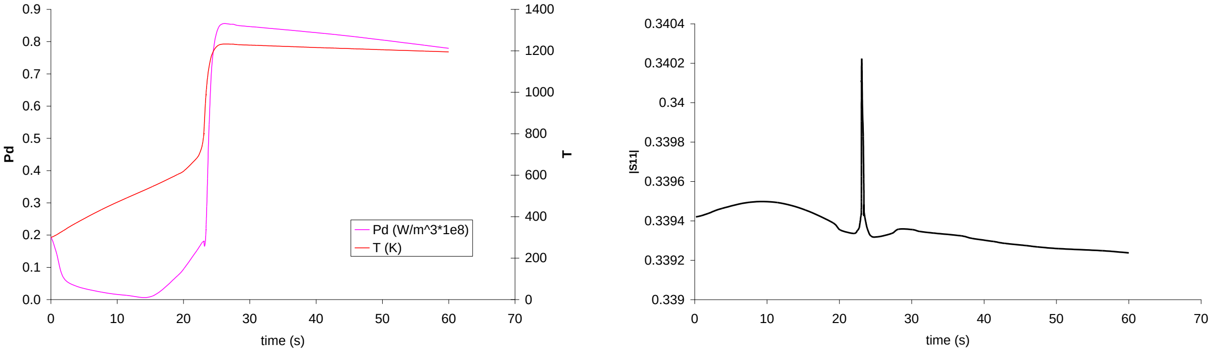
The change of permittivity of the zirconia coating is evident also in the variations of the reflection coefficient of the system, shown in Fig. 3(b), and this also explains the apparently decreasing power density at the very beginning of the heating process ($|S_{11}|$ is increasing).

Rather interestingly, in correspondence of the maximum heating rate, i.e. during CS, numerical simulation indicates a slight increase of the reflection coefficient, despite the zirconia coating becoming lossier at high temperature. This could be ascribed to the variation of the electromagnetic field distribution as a consequence of ε' variations with temperature and to the specific configuration of the microwave applicator. However, the small volume of the zirconia coating can affect the impedance matching only marginally. Moreover, it is experimentally



(a) (b)

Fig. 2. SEM micrographs after concurrent CS and sintering of the samples ZrO_2 coated NiAl (a) and ZrO_2 coated TiAl intermetallics.



(a) (b)

Fig. 3. Power dissipation and temperature evolutions occurring in the ZrO_2 coating as CS of the intermetallic substrate proceeds (a) and $|S_{11}|$ variation as CS proceeds (b).

observed that during CS the power reflected form the load tends to decrease, probably due to the occurrence of breakdown phenomena triggered by the high combustion temperatures favouring the emissions of electrons and gases from the underlying substrate.

Nevertheless, excess heat released by CS reaction ignited by microwaves, or hybrid heating has been also proficiently exploited to promote a further exothermic reaction between metal powders, in order to realize a β-NiAl coated γ-TiAl based alloy in a single combustion synthesis step. The typical product microstructure is reported in the optical micrograph of figure 5 (obtained after etching with a $FeCl_2$ solution).

Conclusions

The use of microwave energy yields unique characteristics in the ignition of combustion synthesis reactions. The excess heat released by the exothermic reaction, leading to the synthesis of the intermetallic substrate, was used to sinter a ceramic zirconia layer previously deposited by means of electrophoretic deposition. A simplified multiphysics model was developed in order to verify that such an excess heat allowed also the zirconia layer to reach a temperature at which it can be directly heated by microwave interaction, as demonstrated by the pronounced increase in the power density distribution as the CS proceeds. The same approach, from both experimental

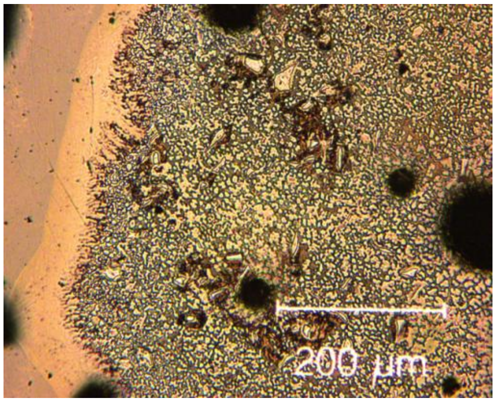


Fig. 5. Optical micrograph of the β-NiAl (left) coated γ-TiAl based intermetallic alloy (right) through a single combustion synthesis experiment in which the heat released by exothermic reaction promoted the ignition of a further CS, allowing the formation of peculiar reaction interface.

and computational viewpoints, was exploited to promote a further CS reaction in order to realize in a single experiment β-NiAl coated γ-TiAl based intermetallic alloy, resulting in a peculiar reaction interface due to the beneficial effects of microwave energy transfer in the extending the existence time of possible liquid phases.

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